AN INVESTIGATION

OF A

MODIFIED BUNSEN ICE CALORIMETER

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED Investigation of a Modified Bunsen Ice Calorimeter

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AN INVESTIGATION OF A MODIFIED BUNSEN ICE CALORIMETER

I. INTRODUCTION

1. Purpose of the Investigation. The purpose of the investigation was to test the action of a modified Bunsen Ice Calorimeter. Theory shows that the Bunsen Calorimeter is promising for the determination of specific heats, but the results of experiments are disappointing, but it appears that the instrument has unexpected defects. It was thought that the modified calorimeter might overcome one of these defects.

2. Calorimetry* Calorimetry is the scientific name for the measurement of heat. There are several different methods used:--method of mixtures, method of cooling, method of condensation, energy methods (mechanical and electrical), and the method of fusion. The Bunsen Ice Calorimeter belongs to the last class. The earlier forms of the ice calorimeter were those of Black and of Laplace and Lavoisier.

a. Black's Calorimeter. Black's Calorimeter consisted of a block of ice with a hole melted out of the center. An object whose specific heat was sought, was heated to steam temperature, inserted in this cavity, and another cake of ice was put over the top for a cover. When the object had come to ice temperature, it was lifted from the cavity and the ice which had melted was absorbed by a weighed cloth which was re-weighed in order to obtain the weight of the ice melted.

*Encyclopedia Brittanica, 11th Ed. Vol.V., page 62

b. The Calorimeter of Laplace and Lavoisier. This calorimeter consisted of a small vessel placed inside of a larger vessel filled with ice. When the hot body was placed in the inner vessel, some of the ice was melted and this was drawn off at the bottom and weighed.

A considerable error is made in measurements with these calorimeters because of the difficulty in determining exactly the amount of ice melted. In the Black Calorimeter, the manipulation with the cloth is likely to melt more ice, while in the Laplace and Lavoisier instrument, the water clings to the ice, due to surface tension. The Bunsen Calorimeter overcomes this uncertainty by measuring the volume melted instead of the weight.

c. Bunsen's Calorimeter. The Bunsen Ice Calorimeter consists of a large test tube T, which is enclosed in a large glass cylinder with a capillary tube extending from the bottom of it up the side. The intervening space between these tubes is filled with pure air,-free water, and mercury. Some of the water around the tube is frozen and since ice occupies more volume than water, some of the mercury is pushed out into the side tube and into the horizontal graduated tube H. When the substance whose specific heat is being measured, is placed in T, some of the ice is melted and the mercury recedes. In order to interpret the indications of the

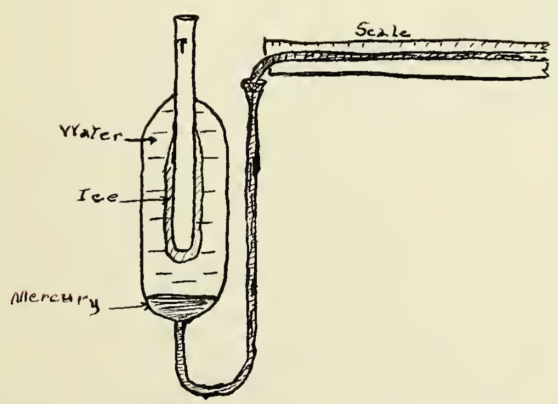


Figure I.

instrument, a known mass of water, m. at a definite temperature, θ, may be introduced into the tube T. In falling to 0° C., this gives out a quantity of heat mθ, and in consequence of the melting of the ice, the mercury in the tube H recedes through n divisions of the scale. This gives the relation between the quantity of heat supplied in any experiment in the tube, T, and the corresponding recession of the mercury along the scale H, for if q is the heat corresponding to each division, we have

$$m\theta = nq.$$

In determining the specific heat of any substance, a fragment of it at room temperature is immersed in the water in the tube T. More ice is melted and the mercury recedes n' divisions of the scale, the whole heat given up by the body in cooling to zero is n'q. Then, if m' be the mass of the body and θ' its original temperature, its specific heat is given by the equation,

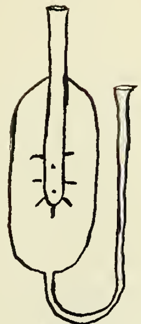
$$m's\theta' = n'q$$

$$\text{hence} \qquad s = \frac{mn'\theta}{m'n\theta'}$$

This all sounds very well until it is tried--then many difficulties are encountered. In the first place, it was suggested and later proved, that a small pocket of ice was melted right around the glass tube, T, by the heat given up by the water and the substance and that the ice was not melted through. If this were the case, the volume would not be changed at all and the mercury in H would not be affected.

The purpose of the investigation was to try to overcome this objection. A new calorimeter was ordered made which had small platinum wires fused in the tube T and extending out into

the water through the ice. Then any heat in the tube T would be conducted along the platinum wires and would melt the ice around



them---thus always melting through to the water and causing the mercury to recede. Also, it seems likely that the ice would form around the wires due to the conduction of the heat along them more rapidly than elsewhere.

Figure 2.

3. Previous Investigations with Bunsen Calorimeters.

a. Bunsen's Work. Robert William von Bunsen invented his ice calorimeter at Heidelberg University in 1870. It was constructed much like the calorimeter described above. The cooling was accomplished by passing cooled alcohol through the tube T. He found that the air freed water inside had to be cooled far below 0° C. before freezing began; the water froze suddenly and was allowed to continue freezing until a cylinder of thickness from six to ten millimeters was formed around the inside tube. The instrument was packed in pure snow which was changed twice daily and the temperature of the room was kept from 5° C. to 6° C. He let the instrument stand a day or two until conditions should become steady before actually performing his experiment. He found that the water was so cooled before freezing began that it would continue to freeze for about 114 hours. For his calculations he used the formula:

$$S = \frac{T}{W} G_t$$

T = number of scale divisions

W = amount of heat given up by one gram of water when cooled from 1° C. to 0° C.

G_t = weight of substance tested

2. Investigation of C. V. Boys. Professor Boys suggested that a protecting cover of glass be provided. If the whole surface of the glass is in contact with the outer snow, the conductivity of heat will be very great if there is a slight difference of temperature between the two sides. The amount of heat passing through the walls of the instrument depends on the difference of temperature and the conductivity, and if both of these factors can be minimized, so much the better. He suggested that the instrument lie in the glass cover and that the two tubes be supported by a thin India rubber cork fitted into the upper end of the glass cover. A third hole in the cork carried a glass tube with a stop-cock. If there was any hurry to cool the instrument, ice-cold water was poured in upon the ice so as to reach above the lower end of the protecting tube, and the stop-cock opened and the air drawn out if necessary until the water reached the cork. This water may be changed. After the water inside the calorimeter was frozen, the water on the outside was drawn out and the instrument was ready for use. It was found that this cover was a decided improvement.

3. Work of J. W. Mellor.* Professor Mellor's contribution was a new method of filling the calorimeter. He says, "The complete separation of dissolved air from the water used in making the 'ice kernel' is necessary for accurate results. At any time the separation of air from water so that the latter will give the characteristic 'click' is a difficult matter, while the filling of the calorimeter with such water is a still more tedious

*J. W. Mellor "Notes on Bunsen's Ice Calorimeter", Journal of Physical Chemistry, Vol. 4, pp. 135-136

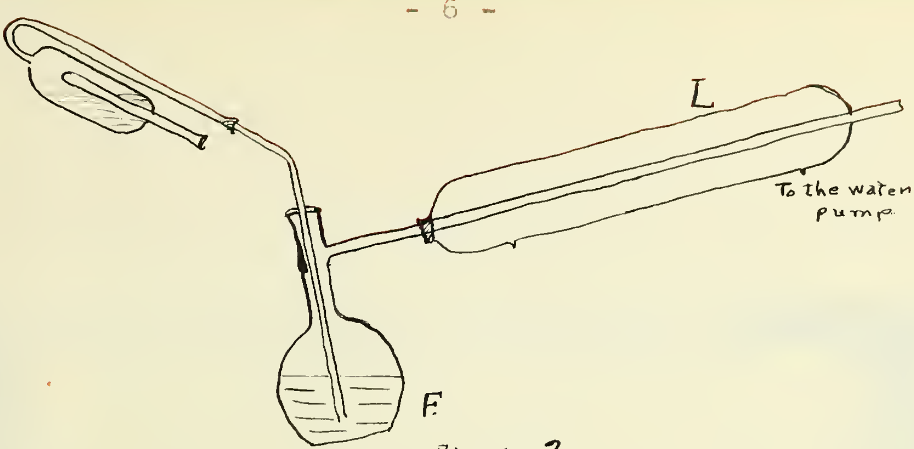


Figure 3

operation. The end of the Liebig's condenser (L), is fitted to the side neck of an ordinary liter distilling flask and the other end is connected to a water air-pump. The flask (F) is about half filled with distilled water, and the outer chamber of the calorimeter is about one third filled with distilled water. A tube dipping almost to the bottom is fitted into the neck of the distilling flask and also into the opening of the side tube of the calorimeter. The pump is set in action, and the water in the calorimeter is heated by a Bunsen flame with a sheet of asbestos placed under it. The flask is heated over a sand bath until its contents give the characteristic hammering when shaken. The lamp is then removed from under the calorimeter and the latter will very soon be filled with air-free water. The troublesome bumping of the water boiling under reduced pressure is considerably modified by the tube dipping under the water in the flask."

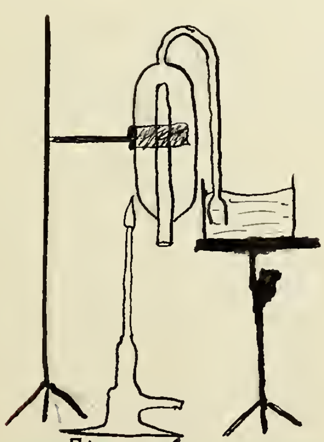


Figure 4

II. THE PRESENT INVESTIGATION

1. Filling the Calorimeter. Probably the most difficult and the most important part of the experiment was to fill the calorimeter with pure air-free water. It was found best to

Figure 6

Figure 6 is a photograph of the apparatus after it is set up ready for use, showing the box in which the calorimeter is packed in snow and the capillary tube extending along the scale.

heat the calorimeter cautiously to drive out some of the air, then to put the open end (O) under some pure distilled, boiled water. As the air cooled and contracted, some of the water was drawn over into the space (S). If this water were boiled vigorously with a Bunsen flame (B), the air in (S) was driven out and the space was filled with vapor. When the flame was removed, this vapor condensed and water was syphoned over into (S) with a great rush filling the space (S). There was always a small bubble of vapor remaining, but if the water were allowed to cool, this contracted to a very small space and if the tube were turned upright very carefully, it ascended the small side tube. Mercury was then poured into the side tube and poked down with an iron wire. This was very clumsy and took a very long time because the water had to push up past the mercury before the mercury could get down. Later, a quicker and more satisfactory method was found by which mercury was poured in to about one-tenth of the volume (S) after the first step in filling (when only a little water was in (S). The mercury did not interfere in the least with the rest of the filling. When the water had cooled and the vapor bubble removed, the side tube was filled with mercury also and the calorimeter was ready for use.

2. Methods of Freezing. The calorimeter which rested on a large cork and some soft wax to prevent breakage, was placed in a metal box made specially for the purpose and was packed in pure shaved ice. A rubber cork fitted in the top of the side tube carried a capillary glass tube which was bent and extended about a meter along a scale. As the water froze, the mercury was pushed from the side tube out along the capillary tube.

a. Calcium Chloride and Ice. The first freezing mixture tried was calcium chloride and shaved ice in the ratio of three parts ice to four parts calcium chloride by weight. A low temperature was not obtained with this because the calcium chloride was not the right sort--crystalline is the kind to be used--and not large enough quantities were mixed at one time. Later crystalline chloride was ground to a powder and mixed with ice. It was found that a temperature of a -8° C. could be obtained in this way, but this was inconvenient to use since the calcium chloride did not dissolve, but sank to the bottom of the tube and could not be syphoned out. It was necessary to turn the calorimeter upside down to get rid of this.

b. Evaporating Ether. A much more convenient method was to put ether in the inner tube (T) and connect it to an aspirator, so that air was bubbled through, the ether thus causing a rapid evaporation and cooling. This did not prove successful. The failure was probably due to the fact that the warm air drawn through the aspirator heated the calorimeter about as fast as it was cooled. Later, the freezing was started with the calcium chloride mixture and then it was attempted to build out the ice with the ether, but it was found that the ice was only melted.

c. Ice and Sodium Chloride. One day, by chance, it was found that if three parts snow to one part sodium chloride were mixed together in large enough quantities, a temperature of a -18° C. could be obtained. This mixture froze the water in the calorimeter very nicely in a short time and was also convenient to clean out after the freezing was accomplished. If the calorimeter were rinsed with water at about 0° C., and thus syphoned out, the

Calorimeter would be clean and ready for use.

3. Results. The calorimeter was then used to find the specific heat of aluminum. First the instrument was calibrated by pouring a weighed amount of water into it and noting how many centimeters the mercury receded. Then a small aluminum coil was placed in the tube so that it was just covered with water. Again the number of centimeters that the mercury receded was observed. Then from the formula

$$S = \frac{mn'\theta}{m'n\theta'}$$

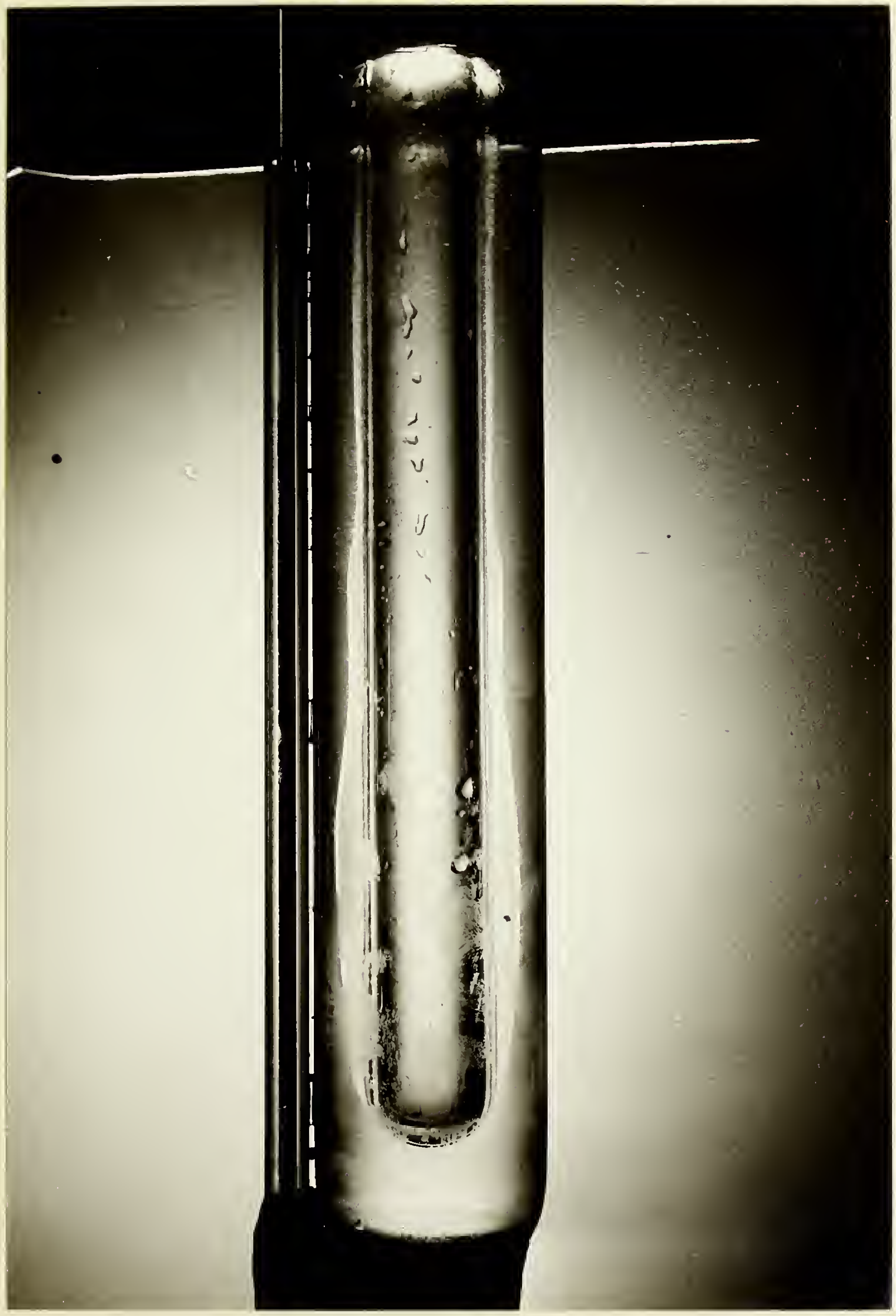
mentioned above, the specific heat of aluminum was calculated.

DATA

	First Trial	Second	Third
Weight of water	3.1321 gms.	5.6565	3.125
Weight of aluminum	3.767	3.7941	3.7941
Divisions of recession for water	7.3 cm.	4.2	1.8
Divisions of recession for al.	1.6	1.9	1.2
Change of temperature of water	23.1° C.	24.5	22.8
Change of temperature of al.	23.5° C.	22.6	22.8
Calculated specific heat	.182	.63	.05

These preliminary results were not good since the accepted value for the specific heat of aluminum is .2143. The same experiment was repeated several times and without concordant results. When an investigation was made to see what was the trouble, it was found each time that just as was expected, a small pocket of water was enclosed between the wall of the tube and the ice around it and that the ice was not melted through. Of course this being the case, no reliable results could be obtained.

Fig. 5 is a photograph of the calorimeter after water is poured to melt the ice. A pocket is shown as suspected between



Fi-ure 5

the glass and the outer coating of ice that would prevent a change in volume and a movement of the mercury column.

The investigation originally planned was not completed. A calorimeter with platinum wires was secured and tried, but it proved to be defective in that the sealing between the wires and the glass was not perfect so that water leaked through. The instrument maker was unable to complete a new calorimeter in time for this investigation.

III. CONCLUSION

The results obtained give promise of showing the effect sought, namely that the ice melts in a pocket around the inner tube so that the outer coating of ice prevents a change in volume of the enclosed water, and the mercury column does not move.

Acknowledgments are due to Professor F. R. Watson who offered the suggestion for the investigation and gave much encouragement and helpfullness to the investigators, and to Miss Vera V. Bassett, my partner in the experiment.

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